

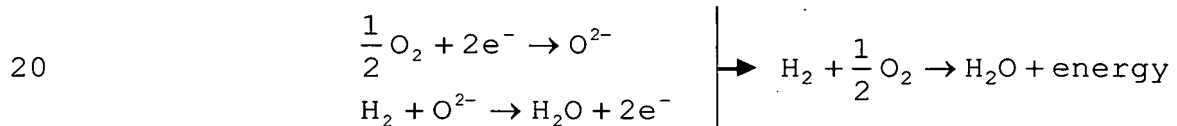
SOLID OXIDE FUEL CELL WITH SEALED STRUCTURE**DESCRIPTION****Technical field and background art**

This invention relates to SOFC type fuel cells, in other words solid oxide fuel cells.

A fuel cell is a system that produces electricity from hydrogen, oxygen and an electrolyte by a catalyst reaction; the electrolyte separates the anode and the cathode while allowing transfer of the ionised species.

There are several types of fuel cell, the main difference being the nature of their electrolyte (liquid, polymer among others). Among these, the solid oxide fuel cell or SOFC has many advantages, including the fact that only two phases are present, namely solid and gas. Its operating temperature (of the order of 900°C) and the heating time are such that this cell is suitable mainly for stationary applications.

As illustrated in Figure 1, an anode (12) and a cathode (14) are separated in SOFCs by a solid electrolyte (16) through which O^{2-} ions produced by the cathode and necessitated by the anode can circulate:



This assembly produces a voltage of the order of 1 volt with a high efficiency.

In order to obtain higher powers for commercial use, several "cells" can be associated in

series or in parallel. This assembly requires that the geometry of each element and the overall architecture should be optimised, particularly for the distribution of gases, recuperation of electricity, etc.

5 One of the envisaged geometries is the tubular architecture: a tube is used as a support for the cathode (at the centre) surrounded by electrolyte plus an anode layer. However, the length of the current lines that it generates causes strong losses by the
10 Joule effect and limits the power output.

 One preferred embodiment is a plane architecture. Cells then have at least two gas inlets and are composed of a stack of plane cells consisting of the triple anode/electrolyte/cathode layer separated
15 by a bipolar plate that collects current and distributes gases.

 For a fuel cell, each anode must be supplied with hydrogen and each cathode must be supplied with oxygen, which particularly in the case of
20 SOFCs, may be pure or mixed, for example in air or in an oxygen enriched air. On the other hand, contact between oxygen and hydrogen must be avoided: they burn, which reduces the performances of the cell, and particularly the mix can explode.

25 Although it may be easy to avoid mixing of the two gases for a single cell, for example by means of a sealed electrolyte that prevents gas transfers, in an assembly of SOFC cells in which individual cells are stacked, it is also important to assure leak tightness
30 between the different cells, regardless of the temperature. Conventional seals no longer act at the

high temperature developed by this type of cell; glass seals have been built specially for this purpose. However, the temperatures reached make the glass seals pasty: after cooling, they are no longer leak tight for
5 a second temperature cycle (if any) in the cell.

Thus, it appears desirable to develop cell architectures that do not need seals, the properties of the new cell assemblies being optimum at the different temperatures that occur during operation of SOFC type
10 fuel cells.

Summary of the invention

The invention provides the means of choosing physical characteristics of materials to overcome problems caused by the use of fuel cells.

15 The invention is also intended to solve leak tightness problems that arise between the different elements of cells used in SOFCs with a plane architecture.

According to one of its aspects, the
20 invention relates to the presence of "compact" areas within a porous electrode layer: these "compact" areas are actually denser or less porous than the remainder of the electrode layer, or are even non-porous at all. In fact, in a fuel cell, the anode and the cathode must
25 enable gas transfer to the electrolyte, and they are therefore porous; creation of zones that are not or only slightly porous then makes it possible to make a duct or a gas inlet, for example by drilling, that can be made leak tight.

Therefore the invention relates particularly to a three-layer structure comprising two porous electrode layers enabling gas transfer, these layers having a first porosity and a second porosity, and a solid electrolyte layer, one of the electrode layers comprising at least one area such that the third porosity is less than the first and the second porosity, referred to in this application as the « compact zone ». Advantageously the third porosity is such that the zone is very slightly porous, in other words the third porosity is very much lower than the first.

The compact zone, in other words that is only slightly or is less porous, in the electrode layer may be placed around the inlet of the first gas that is not intended for this electrode (for example around an oxygen inlet for the anode): this can prevent mixing at this electrode of the first gas with the second gas that circulates in the same electrode to trigger the catalyst reaction.

In particular, the non-porous or slightly porous zone can be created by densification of the porous material of the electrode, and/or by a protuberance of the electrolyte layer, which is dense and gastight, in the electrode layer.

The invention also relates to a fuel cell in which each electrode layer has at least one such area that is non-porous or is only slightly porous, for example for which the electrolyte is thickened and/or the material from which the electrode is made is densified.

These basic elements may be assembled in a cell with a plane architecture. In one of its preferred embodiments, the invention relates to a fuel cell composed of an assembly of cells for which the air or gas inlets are adjacent to areas that are slightly porous or are non-porous, of anodes and hydrogen or gas inlets being adjacent to cathodes in areas that are slightly porous or are non-porous.

According to another aspect, the invention relates to a specific binding between a bipolar plate and an electrode or electrolyte in order to overcome problems caused by gas infiltrations between the electrode and the bipolar plate, or between the electrolyte and the bipolar plate, and therefore to give a good seal. This type of assembly also provides a means of increasing the resistance to shear, particularly when the temperature increases.

Coefficients of thermal expansion of the different ion exchanger elements of the triple layer, usually made of ceramic, are lower than the coefficient of thermal expansion of the bipolar plate which is usually metallic. When the temperature rises due to operation of the cell, this difference may cause loss of mechanical bond between the plate and the cell. Creation of binding between the ceramic and the metal provides a means of limiting creation of passages along which the gases could pass.

Binding is preferably done by nesting of a protuberance of the bipolar plate in a cavity created in the ceramic structure. By seizing the protuberance to correspond to the corresponding cavity, it is

possible to achieve easy assembly at ambient temperature and binding at the cell operating temperature. Advantageously, to improve the mechanical strength, this cavity is located in an area that is non-porous or is slightly porous in the electrode layer as defined above, in other words for example in the extra-electrolyte thickness or in a densified zone of the electrode.

Brief description of the figures

Figure 1 diagrammatically shows the reactions that occur in a basic cell of a fuel cell.

Figure 2 shows an example of a circular plane geometry of a fuel cell made in accordance with the invention.

Figures 3a, 3b and 3c show examples of zones that are non-porous or are slightly porous in electrode layers according to the invention.

Figure 4 diagrammatically shows another sealing defect within the basic cells of a fuel cell.

Figure 5 shows a preferred embodiment of binding around a gas inlet between the bipolar plate and electrode, at ambient temperature (Figure 5a) and at 900°C (Figure 5b).

Figure 6 shows an example embodiment of a plane fuel cell with external headers, in which the proposed two sealing concepts have been integrated.

Detailed description of particular embodiments

Figure 1 diagrammatically shows the operating principle of a fuel cell. As can be seen,

oxygen is used by the cathode (14) to produce O^{2-} ions that react with hydrogen at the anode (12). An oxygen inlet as a chemical element is shown: O_2 is used by the cathode, but the gas inlet (4) in the cell may for example be either an air inlet, or an oxygen enriched air inlet, or a pure oxygen inlet or an inlet of oxygen mixed with any other gas.

The electrodes (12, 14) are porous so that the gases can diffuse and react. On the other hand, the electrolyte (16) only enables O^{2-} ions to diffuse and is dense and leak tight. The energy released is retrieved at the bipolar plates (20), which are usually made of metal. Furthermore, the bipolar plates (20) very often enable distribution of gas through channels created in their structure, and evacuation of water formed by the reactions.

The diagram in Figure 1 also shows a basic cell (5) for the plane architecture of fuel cells (1): a conventional fuel cell consists of a stack of cells (5) according to Figure 1, in parallel or in series, in order to increase the energy quantity produced.

As can be seen in Figure 2, one possibility is the circular plane geometry of the cell (1) with a stack of cells (5). Note that the gas inlets (air and oxygen) (2) define passages that pass through the cells (5) or are adjacent to them so as to reach different electrode layers (12, 14) to enable reactions. Consequently, it can be seen in Figures 1 and 2 that the air passage also passes, for example, through an area in which an anode layer is present, and in which hydrogen circulates. Therefore it is important to have

leak tightness between the air inlet (4) and the anode (12), and similarly for the cathode (14) and the hydrogen inlet (3), in other words in the zone of the electrode adjacent to the gas inlet that is not
5 dedicated to it.

To mitigate the risk of air (in other words oxygen) and hydrogen becoming mixed, the invention proposes to use an electrode layer (10) in which zones that are slightly porous or are non-porous (11), in
10 other words less porous than the remainder of the electrode layer, are created. A porosity of the order of 30% may be suggested for the porous layer and a porosity of less than 6% for dense areas, with a density above 94% of the theoretical density.

Therefore the invention also relates particularly to electrode/electrolyte dual layers in which the electrode layer was chosen locally or made less porous: see Figure 3. Note that only one electrode layer and the electrolyte layer were shown in Figures 3
20 to 5 considering symmetry between the anode and the cathode and to make the figures clearer; obviously, the other electrode and a bipolar layer (20) could be added on these diagrams. For use in SOFC cells, it is desirable to have a zone that is slightly porous or is
25 non-porous (11) for which the dimensions are of the order of a few millimetres over the entire thickness of the electrode (10, 12, 14). It is possible that the porosity of the compact zone (11) will not be constant over the entire thickness of the electrode, wherein a
30 porosity gradient could be created.

For example, the zone that is slightly porous or non-porous (11) can be created by densifying the electrode layer: Figure 3a shows such an embodiment. The densification (13) of the porous material of the electrode, in this case the anode (12), may be made for example by laser. In this case, as above, it is also possible to have a porosity gradient within the layer of material making up the electrode in the direction particular to the displacement direction of the ionic species.

It may be advantageous to use the fact that the electrolyte (16) itself is made of a dense layer, that is non-porous and is gastight. It is thus possible to create an electrolyte protuberance (17), that is inserted in the electrode layer, the cathode (14) in the context of Figure 3b. The protuberances (17) may be made by pouring in strips combined with a thermal compression, or by plasma projection with mask. Advantageously, the protuberance comes into contact with the bipolar plate (20).

The different embodiments may be combined, for example with densification (13) of the electrode layer (10) by prolonging a protuberance (17) of the electrolyte layer (16): Figure 3c.

These zones that are slightly porous or are non-porous can then be used as a support to anchor the bipolar plate (20) as will be described later. Zones that are slightly or are non-porous are preferably used adjacent to gas inlets (2): they may be made around gas inlets (2), particularly in the case of densification (13) of the material from which the electrode is made,

or gas inlets (2) can be drilled after assembly of the different layers necessary for a cell. The two solutions may be used within the same cell. Unlike tubular joints that are sometimes used, these parts are not added on around a gas inlet (2).

Thus, the anode (12) can be densified around or adjacent to air inlets (4) (Figure 3a); for example, the cathode (14) may be protected by an electrolyte protuberance (17) around hydrogen inlets (3) (Figure 3b). These two possibilities are only given for guidance, and it should be understood that each type of manufacturing of areas that are non-porous or are slightly porous, for example densification and/or creation of protuberance(s), is applicable indifferently to each electrode (10), and that they can also be combined within the same cell stack (1), or even the same individual cell (5), for example cathodes (14) protected by densification and anodes (12) protected by electrolyte protuberances (17).

Therefore, use of solutions proposed by the invention improves the leak tightness inside the cells (5).

Furthermore, it might be useful to modify the arrangement between the electrode (10) and the bipolar plate (20) in order to improve the leak tightness, particularly within a stack of cells: in a conventional cell stack (1), individual cells (5) are adjacent to each other but even in the case of a vertical stack, gravity may not be sufficient to hold two successive assemblies sufficiently close to eliminate any gas infiltration. The problem may arise

particularly for the junction (6) between the bipolar plate (20) and the electrode (10) and/or the electrolyte (16): see Figure 4.

As mentioned above, the bipolar plate (20) collects released energy and is conducting, and is therefore often metallic; the electrodes (10) are made of porous material, often ceramic, which is also the material used for the electrolyte (16).

In particular, the two types of material have a different behaviour under heat, and temperatures in SOFC cells are high. It is indeed conventional to have coefficients of thermal expansion of the order of $10 \times 10^{-6}/K$ for the electrolyte, and $15.7 \times 10^{-6}/K$ for the bipolar plate, knowing that the temperature reaches $900^{\circ}C$. Since the thermal expansion of the bipolar plate (20) is higher than the thermal expansion of the electrode (10) or the electrolyte (16), shear forces are created at the junction (6) between the bipolar plate and its support, and these forces can cause rupture.

It is possible to take advantage of this difference in behaviour by binding using a male/female type layout, with nesting between the bipolar plate (20) and the subjacent ceramic layer (10, 16).

Thus, protuberances (22) can be created on the surface of the bipolar plate (20) facing the ceramic. Cavities (18) are made in the ceramic layer (10, 16), for example by machining, so that the protuberances (22) of the bipolar plate (20) can be nested: see Figures 5. The protuberances (22) of the bipolar plate may be made by machining, or may be made

by pouring in strips combined with thermal compression, or by plasma projection with mask.

Preferably, the cavities (18) are larger in width and/or in depth than the size of the corresponding protuberances (22) at the ambient temperature, therefore leaving an assembly clearance (Figure 5a). In this way, when the temperature increases, the greater expansion of the bipolar plate (20) than the electrolyte (16) and/or the electrode (10) will anchor the protuberance (22) of the bipolar plate into the cavity (18) (Figure 5b), and will assure leak tightness without creating any additional stress. Therefore, this principle further improves the mechanical behaviour of the cell at high temperature.

Preferably, and as shown in Figures 5a and 5b, the assembly (18, 22) is made along the gas inlets (2), or the air or hydrogen inlets, in the layers of cells (5) in the fuel cell.

It is advantageous to create cavities (18) in one or more of the areas that are non-porous or are slightly porous (11) of the electrodes (10), as described in one of the previous embodiments.

In particular, if the electrode (10) has a compact zone (11) that corresponds to a protuberance (17) of the electrolyte (16), it is preferred to create the cavity (18) in this protuberance, and to not change the rest of the electrode (10) in order to keep the efficiency optimum. Cavities may also be present for assembly within the electrode layer, even if it is not densified.

The described modifications to the assembly, namely creation of zones in the electrode layer that are non-porous or are slightly porous, the use of such a slightly porous zone, or a protuberance of the electrolyte about gas inlets and creation of binding, can increase leak tightness and improve mechanical behaviour at high temperature. They can be applied for circular plane geometries like those shown in Figure 2, but also for rectangular or square geometries such as stacked plates, or in structures designed around external headers (Figure 6). The gas feed may be made through an external header, or the header may be formed by the stack of plates.